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DescriptionPRE-PAINT TREATMENT OF METAL AND PRODUCT THEREOF*JNS A*

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to a pre-paint aqueous treatment agent which is used to make functionally surface treated steel sheets that are variously known as "colored", "painted", or "PCM" steel sheets, a process for manufacturing such a functionally surface treated metal material with superior adhesion using this pre-paint aqueous treatment agent, and a metal material so made.

Functionally surface treated steel sheets are used in household electrical appliances, construction materials, automobiles, etc. Such steel sheets are covered with an organic coating film after the metal substrate has been subjected to a chromate conversion coating treatment; accordingly, such plates have superior design properties in addition to superior workability and corrosion resistance. However, as concern for the protection of the global environment has increased in recent years, the movement to avoid the use of substances harmful to the human body (in the case of colored steel sheets, hexavalent chromium contained in the undersurface and organic coating film) has become stronger. Recently, therefore, there has been an increased demand for chromium-free (non-chromate type) undersurface treatment agents and chromium-free (non-chromate type) organic coating film agents.

Conventional techniques relating to such agents are disclosed in Japanese Patent Application Kokai No. 59-116381 and Japanese Patent Application Kokai No. 4-66173, etc. The technique disclosed in Japanese Patent Application Kokai No. 59-116381 is a process in which zinc and zinc alloy surfaces are treated with an aqueous solution that contains tannic acid and a silane coupling agent, and a coating film is formed on these surfaces. However, since tannic acid is soluble in water, the adhesion that is the goal of this invention cannot be obtained in the case of coating films produced by this process. The technique disclosed in Japanese Patent Application Kokai No. 4-66173 relates to metal sheets in which the surfaces of aluminum-plated metal sheets or aluminum plates are coated with a treatment solution whose essential components are one or more compounds selected from a set consisting of fluorine compounds of titanium or zirconium, and one or more agents selected from a group consisting of silane coupling agents that have amino groups, epoxy groups or mercapto groups, after which this coating is dried and a heat-resistant resin containing sulfur atoms is formed on top of this coating. The metal sheets obtained by this process have a superior heat resistance; however, the adhesion that is the goal of this invention cannot be obtained.

Thus, under current conditions, conversion coating films with superior corrosion resistance and adhesion which can be used as pre-paint undersurfaces instead of chromate conversion coating films cannot be obtained using any process known to the applicants.

5 Major objects of the present invention are to provide a pre-paint aqueous treatment agent which can form a coating film that has superior corrosion resistance and paint adhesion properties on the surface of a metal material, a process for manufacturing a metal substrate coated using this pre-paint aqueous treatment agent, and an article of manufacture including such a coated metal material substrate.

10 BRIEF SUMMARY OF THE INVENTION

Suh Ad ~~It has been discovered that a coating film possessing not only corrosion resistance but also superior adhesion can be formed by treating the surface of a metal material with an aqueous treatment agent that contains a specified resin, a silane coupling agent and fine particles with a particle size of 1.0 millimeter (hereinafter usually abbreviated as "mm") or smaller. This discovery led to the present invention.~~

15 DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

20 Specifically, the pre-paint aqueous liquid treatment agent of the present invention, which has superior adhesion, is characterized by the fact that said agent comprises, preferably consists essentially of, or more preferably consists of, water and the following components:

- (a) from 20 to 70 percent by weight of a component selected from a group consisting of urethane resins, epoxy resins, and acrylic resins;
- (b) from 10 to 60 percent by weight of a component of silane coupling agent; and
- (c) from 10 to 40 percent by weight of a component of dispersed solid particles with a mean particle size of 1.0 μm or less,

25 all of the percentage values specified above for components (a), (b), and (c) being percentage of the non-volatiles content of the treatment agent only.

30 In a process of the present invention, at least one surface of a metal substrate, which may optionally have been previously subjected to a chemical plating treatment or a phosphate conversion coating treatment is coated with a liquid layer of the aforementioned pre-paint aqueous treatment agent, and later, usually preferably more or less immediately after the liquid coating layer has been formed, the liquid coating is dried, without any of the non-volatile content of the liquid layer having been removed by any method other than volatilization, e.g., by rinsing with another liquid. A dry coating film thus formed preferably has a mass per unit area coated, a value often referred to as "coating weight", that is from 0.05 to 1.0 grams of dry coating per square meter of

surface coated, this unit of coating weight being applicable to any kind of coating and being hereinafter usually abbreviated as "g/m²".

Moreover, an article of manufacture according to the invention is characterized by the fact that said article of manufacture includes a surface made by the aforementioned manufacturing process.

Any urethane resins that constitute all or part of component (a) as described above preferably contain hydrophilic moieties such as carboxyl moieties, hydroxy moieties or amino moieties, etc., as functional moieties. There are no particular restrictions on the process of manufacture used for the resins. Suitable processes include auto-emulsification processes in which an aqueous system is formed using the aforementioned hydrophilic functional moieties and emulsion polymerization processes using surfactants. Examples of such urethane resins that are commercially available include SUPERFLEX 90, 107M, 110, 130, 150, 300, 410, 700, and 820 resins manufactured by Daiichi Kogyo Seiyaku K.K.; ADEKABONTIGHTER HUX-550, HUX-232, HUX-670, and HUX-293 resins manufactured by Asahi Denka Kogyo K.K.; and PERMALIN UA-200 and UA-300 resins manufactured by San'yo Kasei Kogyo K.K.

Examples of preferable epoxy resins for component (a) include resins obtained by reaction of epichlorohydrin with at least one of bisphenol-A, bisphenol-F, hydrogenated bisphenol-A, and novolak type phenol-formaldehyde resins. There are no particular restrictions on the process of manufacture used for these resins, and the same techniques as noted above for urethane resins are also applicable for epoxy resins. Examples of commercially available suitable resins include EPI REZ 3519W50, 3522W60, 3540WY55, 3551WY43, 5003W55, and 6006W70 resins manufactured by Yuka Shell Epoxy K.K. and ADEKARESIN EPE-0410 and EPE-0425W resins manufactured by Asahi Denka.

Any acrylic resins used in component (a) as described above preferably contain (meth)acrylic acid or a derivative of (meth)acrylic acid as their chief component. There are no narrow restrictions on the process of manufacture used; however, it is preferable that the process used be an emulsion polymerization process using a surfactant emulsifying agent, more preferably a copolymerizable emulsifying agent such as sulfoethyl acrylate. Examples of commercially available resins of this type include PRIMALL K-3, TR-934, HA-8, NW-1402, NW-1715, E-693, and E-1242E resins manufactured by Rohm and Haas Co.; MOVINYL 860, 940, 700, 709, 745, and 931 resins manufactured by Hoechst Gosei K.K.; and BONCOAT 3625, 3660K, EC-863, EC-898, EC-818, EC-840, EC-846, and EC-856 resins manufactured by Dai-Nippon Inki Kagaku Kogyo K.K.

The non-volatile content of component (a) preferably is from 25 to 65 percent by

weight, or more preferably 30 to 60 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the liquid treatment agent. If the non-volatiles content of component (a) is less than 20 percent by weight relative to 100 percent by weight of the total non-volatiles content, the retention power of component (c) in the coating film drops so that the corrosion resistance drops, which is undesirable. On the other hand, if the non-volatiles content of component (a) exceeds 70 percent by weight, the relative proportions of component (b) and component (c) drop so that there is a drop in the corrosion resistance and adhesion, which is also undesirable.

It is desirable that the silane coupling agent of component (b) used in the present invention be a compound which has functional moieties that possess reactivity with the resin. Examples of such silane coupling agents include vinyltrichlorosilane, vinyltrimethoxsilane, vinyltriethoxsilane, vinyltris(β-methoxyethoxy)silane, β-(3,4-epoxycyclohexyl)-ethyltrimethoxsilane, γ-glycidoxypolytrimethoxsilane, γ-glycidoxypolytriethoxsilane, γ-methacryloxypropylmethyldimethoxsilane, γ-methacryloxypropyltrimethoxsilane, γ-methacryloxypropylmethyldiethoxsilane, γ-methacryloxypropyltriethoxsilane, N-β-(aminoethyl)-γ-aminopropylmethyldimethoxsilane, N-β-(aminoethyl)-γ-aminopropyltrimethoxsilane, N-β-(aminoethyl)-γ-aminopropyltriethoxsilane, γ-aminopropyltrimethoxsilane, γ-aminopropyltriethoxsilane, N-phenyl-γ-aminopropyltrimethoxsilane, γ-chloropropyltrimethoxsilane and γ-mercaptopropyltrimethoxsilane. Furthermore, the silane coupling agent component used in the present invention may also consist of two or more coupling agents used in combination.

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The non-volatiles content of component (b) preferably is at least, with increasing preference in the order given, 15, 18, 20, 22, or 24 percent by weight and independently preferably is at least, with increasing preference in the order given, 50, 40, 38, or 36 percent by weight of the total non-volatiles content. If the non-volatiles content of component (b) is less than 20 percent by weight relative to 100 percent by weight of the total non-volatiles content, the adhesion of the coating film drops, as is undesirable. On the other hand, if the non-volatiles content of component (b) exceeds 60 percent by weight, the relative proportion of component (a) in the coating film drops, so that the corrosion resistance drops, as is also undesirable. Good practical results are facilitated by a concentration within the more preferred ranges.

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Component (c) preferably is selected from the group consisting of plastic pigments, phosphorus-containing anti-rust pigments, and colloidal-sized silica (including fumed silica), alumina, zirconia, and titania. It is more preferable if any silica, alumina, zirconia, or titania used for component (c) has in fact been prepared as a stable colloid dispersed in a fluid continuous phase. If the mean particle size of component (c) ex-

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cont.*

ceeds 1.0 mm, some of the particles are likely to protrude from the surface of the coating film; as a result, moisture may easily invade the surface of the material from the particle interfaces, thus causing a drop in corrosion resistance and adhesion. Accordingly, such a large mean particle size is undesirable.

5 Examples of commercially available fine particles with a mean particle size of 1.0 μm or less that are suitable for component (c) include the following: SNOWTEX 20, 30, 40, 50, C, N, O, S, 20L, L, UP, OUP, XL, YL, ZL, P-1040, MP-3040, MP-4540, AK, and BK and QAS 40 and 25 colloidal dispersions of silica in water, all manufactured by Nissan Kagaku Kogyo K.K.; AEROSIL 130, 200, 300, 380, TT600, MOX80, and MOX170 10 fumed silicas manufactured by Nippon Aerosil K.K.; ALUMINA-SOL 100, 200, 520 dispersions of alumina in water manufactured by Nissan Kagaku Kogyo K.K.; NZS -20A, -30A, and -30B dispersions of zirconia in water manufactured by Nissan Kagaku Kogyo K.K.; pulverized zinc phosphate, aluminum phosphate, and calcium phosphate as examples of phosphorus-containing rust-inhibiting pigments; and MUTICLE 100P and 15 240D plastic pigments manufactured by Mitsui Kagaku K.K., ROPAQUE OP-62 and HP-91 plastic pigments manufactured by Rohm and Haas Co., and MP-1000, -1100, -1201, -1450, -1451, -1600, -2701, -3100, and -4009 plastic pigments manufactured by Soken Kagaku K.K. Furthermore, component (c) may also consist of a mixture of two or more types of particles.

20 The solids content of component (c) preferably is from 10 to 35 percent by weight, or more preferably 10 to 30 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the aqueous liquid treatment. (Because component (c) is defined to be dispersed solids, its solids content is the same as its non-volatiles content.) If the solids content of component (c) is less than 10 percent by weight relative 25 to 100 percent by weight of the total non-volatiles content, the adhesion drops. Accordingly, such a small solids content is undesirable. On the other hand, if the solids content of component (c) exceeds 40 percent by weight, the coating film becomes hard and brittle so that the corrosion resistance and adhesion drop. Accordingly, such a large solids content is also undesirable.

30 The pH of the pre-paint aqueous treatment agent of the present invention is preferably in the range of 2 to 10, and is even more preferably in the range of 2.5 to 9.5. If the pH of the treatment agent is less than 2, there is a danger that the metal substrate will be etched and that the corrosion resistance will drop. Accordingly, such a low pH is undesirable. On the other hand, if the pH exceeds 10, the alkali component remaining 35 in the coating film usually causes a drop in the water resistance. Accordingly, such a high pH is also undesirable. Furthermore, there are no narrow restrictions on the

material used to adjust the pH of the treatment agent. However, if the pH is to be adjusted to the acidic side, it is desirable to use at least one substance selected from the group consisting of: organic acids, such as formic acid, acetic acid, butyric acid, oxalic acid, succinic acid, lactic acid, L-ascorbic acid, tartaric acid, citric acid, DL-malic acid, 5 malonic acid, maleic acid, and phthalic acid; phosphoric acids, such as meta-phosphoric acid, pyrophosphoric acid, ortho-phosphoric acid, triphosphoric acid or tetraphosphoric acid; and fluorine-containing acids, such as hexafluorozirconic acid, hexafluorotitanic acid, hexafluorosilicic acid, and hydrofluoric acid. If the pH is instead to be adjusted to the alkaline side, it is preferable to use ammonia or amine compounds such as 10 methylamine, ethylamine, propylamine, isopropylamine, butylamine, amylamine, dimethylamine, diethylamine, dipropylamine, diisopropylamine, trimethylamine, triethylamine, tripropylamine and/or triisopropylamine.

The concentration of the non-volatiles content in the pre-paint aqueous treatment agent of the present invention preferably is in a range of from 0.1 to 50 %. If the concentration of the non-volatiles content is less than 0.1%, it is difficult to obtain the desired amount of coating film; on the other hand, if the concentration of the non-volatiles content exceeds 50 %, it becomes difficult to adjust the treatment agent because of its high viscosity, so that such a large non-volatiles content is undesirable. More preferably, to facilitate practical achievement of a desired coating weight, the concentration of the non-volatiles content is at least, with increasing preference in the order given, 0.5, 1.0, 20 2.0, 3.0, 3.5, or 3.9 % and independently preferably is not more than, with increasing preference in the order given, 40, 30, 20, 15, 12, 10, 8, or 6 %.

Metal materials on which the pre-paint aqueous treatment agent of the present invention can be used include steel, e. g., cold-rolled steel sheets and hot-rolled acid-washed plates; galvanized steel sheets, e. g., zinc-electroplated steel sheets, melt-galvanized steel sheets, alloyed galvanized steel sheets, aluminum-containing galvanized steel sheets, zinc-nickel-plated steel sheets, zinc-cobalt-plated steel sheets and vacuum-deposition type galvanized steel sheets; and aluminum and predominantly aluminum alloys.

30 Leveling agents, viscosity enhancing agents and film-forming assistants, etc., commonly used in aqueous treatment agents may also optionally be added to the pre-paint aqueous treatment agent of the present invention.

When directly applied to the surface of a metal and then dried, the pre-paint aqueous treatment agent of the present invention can endow the metal material with a 35 superior corrosion resistance and adhesion; however, such a metal material can be endowed with an even more superior corrosion resistance and adhesion by subjecting

the material to a chemical plating treatment or a phosphate formation treatment and then applying a treatment agent according to this invention over this precoating. There are no narrow restrictions on chemical plating processes that can be used, but it is preferred to plate iron, cobalt, and/or nickel and independently to have a plating coating weight of 5 1 to 50 milligrams per square meter of surface treated (hereinafter usually abbreviated as "mg/m²"), calculated as elemental metal. Similarly, there are no narrow restrictions on the type of phosphate conversion coating processes that can be used, but it is preferable to use a zinc phosphate conversion coating with a coating weight in the range from 0.5 to 3 g/m².

10 The amount of coating film from a treatment according to the invention preferably is from 0.05 to 0.5 g/m². If the amount of coating film that is formed is less than 0.05 g/m², the corrosion resistance and adhesion are usually insufficient. Accordingly, such a small amount of coating film is undesirable. On the other hand, if the amount of coating film exceeds 1.0 g/m², cohesive failure of the coating film itself tends to occur 15 more frequently, so that there is a danger that the adhesion will drop. Accordingly, such a large amount of coating film is undesirable.

20 There are no narrow restrictions on the process used to apply the pre-paint aqueous treatment agent of the present invention directly to the surface of the metal material or the process used to dry said pre-paint aqueous treatment agent. Examples of suitable coating processes include roll coating, immersion, and electrostatic coating. Examples of suitable drying processes include forced hot air and induction heating. Independently, it is desirable that the highest temperature reached by the metal substrate during drying be in the range from 50 to 250 °C, and a temperature in the range from 60 to 220 °C is even more preferable.

25 There are no narrow restrictions on the paint that is applied to the surface of the metal material that has been subjected to a pre-paint treatment using the pre-paint aqueous treatment agent of the present invention. Examples of suitable paints include those containing conventional chromic acid type anti-rust pigments, phosphate type anti-rust pigments, molybdate type anti-rust pigments, finely powdered silica, and other metal 30 oxide pigments such as TiO₂, and the paints may also contain other coloring pigments. Furthermore, one or more further coatings, the last of which is usually called a "top coat", may be applied over the ordinary primer or other first coat applied directly to the surface formed by a process according to the invention. There are no narrow restrictions on the types of paints used in such top coats. Suitable examples include all of epoxy resin type, 35 polyester resin type, acrylic resin type, urethane resin type, alkyd resin type, and fluororesin type paints.

The present invention may be further appreciated by consideration of the working examples of the present invention and comparative examples presented below. However, the scope of the present invention is not limited by these working examples.

5 The test samples, pretreatments and pre-paint aqueous treatment agent coating processes used in the following working examples and comparative examples are described below.

1. Preparation of Test Samples

(1-1) Tested Metal Substrates

10 The commercially marketed materials indicated below, with short codes used to identify the substrates in a table below following each type in parentheses, were used as test materials:

Melt-galvanized steel sheets ("GI") — Sheet thickness = 0.5 millimeter (hereinafter usually abbreviated as "mm"), coating weight = 90/90 g/m²;

15 Melt-galvanized steel sheets containing 5 % aluminum in the galvanizing coating ("GF") — Sheet thickness = 0.5 mm, coating weight = 90/90 g/m²;

Melt-55 %-zinc-45 % aluminum galvanized steel sheets ("GL") — Sheet thickness = 0.8 mm, coating weight = 90/90 g/m²;

A-1100 type aluminum plates ("AL") — Sheet thickness = 0.8 mm.

(1-2) Degreasing Treatment

20 The test substrates were subjected to a spray treatment for 2.0 minutes at a temperature of 60 °C, using as degreaser a solution in water of FINECLEANER® 4336 alkaline degreasing agent concentrate (commercially available from Nihon Parkerizing Co., Ltd., Tokyo) at a concentration of 20 grams of the concentrate per liter of degreasing agent, this unit of concentration being freely used hereinafter for any constituent of any liquid and being usually abbreviated as "g/l". The test substrates were then washed for 25 30 seconds with pure water and dried.

(1-3) Pretreatments

(1-3-1) Chemical Plating Treatment

30 The test substrates which had been subjected to the abovementioned degreasing treatment were subjected to a spray treatment at a concentration of 100 g/l and a temperature of 50 °C, using PREPALENE® 4015 chemical nickel plating liquid (commercially available from Nihon Parkerizing Co., Ltd.). The test substrates were then washed for 30 seconds with deionized water and dried. The amount of adhering nickel was found to be 20 mg/m².

(1-3-2) Phosphate Formation Treatment

Test substrates which had been subjected to the abovementioned degreasing treatment were dipped for 10 seconds at a temperature of 30 °C in a solution containing 1.0 g/l in water of PREPALENE® Z surface conditioning agent concentrate (manufactured by Nihon Parkerizing Co., Ltd.). Afterward, the test substrates were subjected to a dipping treatment at a temperature of 60 °C in a solution in water of 60 g/l of PAL-BOND® L3300 phosphate conversion coating agent (manufactured by Nihon Parkerizing Co., Ltd.). The test substrates were then washed for 30 seconds with deionized water and dried. The amount of phosphate conversion coating was 2 g/m².

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(1-4) Application of Surface Treatment Agents According to the Invention

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The pre-paint aqueous treatment agents described below were applied by means of a bar coater, and were dried at a temperature of 300 °C.

2. Preparation and Constitution of the Aqueous Pre-Paint Treatment Agents

(Note: All "parts" and percentages stated below are by weight.)

Treatment Agent A

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Amounts of 100 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K. to supply component (a), 35 parts of γ -glycidoxypolypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. to supply component (b), and 150 parts of SNOWTEX 20 (concentration of solids 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K. to supply component (c) were measured and mixed with 1710 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of ammonia. The part of the total non-volatiles content of the treatment solution that was component (a) was 35 percent, the part of total non-volatiles content of the treatment solution that was component (b) was 35 percent, and the part of total non-volatiles content of the treatment solution that was solids content of component (c) was 30 percent. The concentration of the total non-volatiles content of the treatment solution was 5.0 %.

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Treatment Agent B

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Amounts of 100 parts of EPI REZ 5003W55 (concentration of non-volatiles content 55 %) epoxy resin manufactured by Yuka Shell Epoxy K.K. to supply component (a), 25 parts of N- β -(aminoethyl)- γ -aminopropylmethyldimethoxysilane (concentration of non-volatiles content 100%) manufactured by Toshiba Silicone K.K. to supply component (b), and 100 parts of ZIRCONIA-SOL NZS-20A (concentration of solids content 20%) zirconia sol manufactured by Nissan Kagaku K.K. to supply component (c) were measured out and dispersed in 2275 parts of deionized water by means of propeller agitation. The

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pH of this treatment solution was adjusted to 4 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of acetic acid. The weight of the non-volatiles content of component (a) was 55 percent by weight, the weight of the non-volatiles content of component (b) was 25 percent by weight, and the weight of the solids content of component (c) was 20 percent by weight, all relative to 100 percent by weight of the total non-volatiles content of the treatment solution, and the total concentration of the non-volatiles content of the treatment solution was 4 %.

Treatment Agent C

Amounts of 100 parts of PRIMALL K-3 (concentration of non-volatiles content 46 %) acrylic resin manufactured by Rohm and Haas Co. to supply component (a), 20 parts of γ -mercaptopropyltrimethoxsilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. as component (b), and 94 parts of SNOWTEX OUP (concentration of non-volatiles content 15 %) colloidal silica manufactured by Nissan Kagaku Kogyo K.K. to supply component (c) were measured out and dispersed in 2286 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 9 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of triethylamine. The weight of the non-volatiles content of component (a) was 58 percent by weight, the weight of the non-volatiles content of component (b) was 25 percent by weight and the weight of the solids content of component (c) was 17 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. The concentration of the total non-volatiles content of the treatment solution was 4 %.

Treatment Agent D

Amounts of 80 parts of EPI REZ 5003W55 (concentration of non-volatiles content 55 %) epoxy resin manufactured by Yuka Shell Epoxy K.K. and 60 parts of FINETEX ES-2200 (concentration of non-volatiles content 25 %) epoxy resin manufactured by Dai-Nippon Inki Kagaku Kogyo K.K. to jointly supply component (a), 31 parts of γ -glycidoxypropyltrimethoxsilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. to supply component (b), and 100 parts of ALUMINA-SOL 100 (concentration of solids content 10 %) alumina sol manufactured by Nissan Kagaku Kogyo K.K. to supply component (c) were measured out and dispersed in 729 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 3 by the dropwise addition of an appropriate amount of a 5 % aqueous solution of phosphoric acid. The weight of the non-volatiles content of component (a) was 59 percent by weight, the weight of the non-volatiles content of component (b) was 31 percent by weight, and the weight of the solids content of component (c) was 10

percent by weight, all relative to the total non-volatiles content of the treatment solution. The concentration of the non-volatiles content of the treatment solution was 10 %.

Treatment Agent E

Amounts of 100 parts of PRIMAL K-3 (concentration of non-volatiles content 46 %) acrylic resin manufactured by Rohm and Haas Co. to supply component (a), 10 parts of γ -glycidoxypolytriethoxysilane (concentration of non-volatiles content 100 %) and 10 parts of γ -chloropropyltrimethoxysilane (concentration of non-volatiles content 100 %) both manufactured by Toshiba Silicone K.K. were measured out to supply component (b), and 32 parts of MUTICLE 240D (concentration of non-volatiles content 44 %) plastic pigment manufactured by Mitsui Kagaku K.K. to supply component (c) were measured out and dispersed in 1098 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The weight of the non-volatiles content of component (a) was 58 percent by weight, the weight of the non-volatiles content of component (b) was 25 percent by weight and the weight of the non-volatiles content of component (c) was 17 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. The concentration of the total non-volatiles content of the treatment solution was 8 %.

Comparative Treatment Agent F

Amounts of 35 parts of γ -glycidoxypolytriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. and 150 parts of SNOW-TEX 20 (concentration of non-volatiles content 20 %) colloidal silica manufactured by Nissan Kagaku Kogyo K.K. were measured out and dispersed in 1115 parts of water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. This treatment solution did not contain any material corresponding to component (a) of a treatment composition according to this invention.

Comparative Treatment Agent G

Amounts of 100 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K. and 150 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica manufactured by Nissan Kagaku Kogyo K.K. were measured out and dispersed in 1050 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. This

treatment solution did not contain any material corresponding to component (b) of a treatment solution according to this invention.

Comparative Treatment Agent H

Amounts of 100 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K. and 35 parts of γ -glycidoxypolypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K. were measured out and dispersed in 1265 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. This treatment solution did not contain any material corresponding to component (c) of a treatment solution according to this invention.

Comparative Treatment Agent I

Amounts of 220 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 13 parts of γ -glycidoxypolypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 50 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica manufactured by Nissan Kagaku Kogyo K.K., were measured out and dispersed in 1717 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 77 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 13 percent by weight, and the weight of the non-volatiles content of the material corresponding to component (c) was 10 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of the material corresponding to component (a) exceeded the upper limit specified for a composition according to this invention.

Comparative Treatment Agent J

Amounts of 40 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 46 parts of γ -glycidoxypolypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 200 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K.

were measured out and dispersed in 1714 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 14 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 46 percent by weight, and the weight of the non-volatiles content of the material corresponding to component (c) in a composition according to this invention was 40 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of component (a) was below the lower limit specified for a composition according to this invention.

Comparative Treatment Agent K

Amounts of 200 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 5 parts of γ -glycidoxypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 125 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K., were measured out and dispersed in 1670 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 70 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 5 percent by weight, and the weight of the non-volatiles content of the material corresponding to component (c) in a composition according to this invention was 25 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was below the lower limit specified for a composition according to this invention.

Comparative Treatment Agent L

Amounts of 60 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 64 parts of γ -glycidoxypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 75 parts of SNOWTEX 20 (concentration of non-

volatiles content 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K., were measured out and dispersed in 1801 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the 5 non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 21 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 64 percent by weight, and the weight of the non-volatiles content of the material 10 corresponding to component (c) in a composition according to this invention was 15 percent by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention exceeded 15 the upper limit specified for a composition according to this invention.

Comparative Treatment Agent M

Amounts of 220 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 18 parts of γ -glycidoxypropyltriethoxysilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 25 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K., were measured out and dispersed in 1737 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles 20 content of the material corresponding to component (a) in a composition according to this invention was 77 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 18 percent by weight and the weight of the non-volatiles content of the material corresponding to component (c) in a composition according to this invention was 5 percent 25 by weight, relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of the material corresponding to component (c) in a composition according to this invention was below 30 the lower limit specified for a composition according to this invention.

Comparative Treatment Agent N

Amounts of 100 parts of SUPERFLEX 700 (concentration of non-volatiles content 35 %) urethane resin manufactured by Daiichi Kogyo Seiyaku K.K., 15 parts of γ -gly-

cidoxypropyltriethoxsilane (concentration of non-volatiles content 100 %) manufactured by Toshiba Silicone K.K., and 250 parts of SNOWTEX 20 (concentration of non-volatiles content 20 %) colloidal silica dispersion manufactured by Nissan Kagaku Kogyo K.K., were measured out and dispersed in 1635 parts of deionized water by means of propeller agitation. The pH of this treatment solution was adjusted to 8 by the dropwise addition of an appropriate amount of 5 % aqueous ammonia. The concentration of the non-volatiles content of this treatment solution was 5 %. The weight of the non-volatiles content of the material corresponding to component (a) in a composition according to this invention was 35 percent by weight, the weight of the non-volatiles content of the material corresponding to component (b) in a composition according to this invention was 10 15 percent by weight, and the weight of the non-volatiles content of the material corresponding to component (c) was 50 percent by weight, all relative to 100 percent by weight of the total non-volatiles content of the treatment solution. Thus, the weight of the non-volatiles content of the material corresponding to component (c) exceeded the upper 15 limit specified for a composition according to this invention.

3. Processes Used to Further Coat Test Substrates after Treating Them with a Treatment Solution According to the Invention.

The respective treated substrates prepared in the working examples and comparative examples were coated with a commercially marketed undercoat paint (V NITTO #200 manufactured by Dai-Nippon Toryo K.K.) (film thickness: 5.5 µm) and were baked at 200 °C. Then, a top coat paint (V NITTO # 500 manufactured by Dai-Nippon Toryo K.K.) was applied (film thickness: 17 µm), and this was baked at 220 °C, thus producing the coated substrates subjected to the tests noted below.

4. Evaluation Tests

4.1 Corrosion Resistance Test

Scratches that reached the metal material were formed in the coating films by means of a cutter, and the salt water spray test stipulated in Japanese Industrial Standard (hereinafter usually abbreviated as "JIS") Z2371 was performed for 480 hours. The width (in mm) of the rust extending from the cut parts was measured as an evaluation criterion and is reported in tables below on the following scale:

◎: less than 3 mm

O: 3 mm or greater, but less than 5 mm

Δ: 5 mm or greater, but less than 10 mm

X: 10 mm or greater.

4.2 Folding Adhesion Tests

4.2.1 Primary Folding Adhesion Test

In accordance with the test process described in JIS-G3312, the respective test coated substrates were subjected to a 2T folding test with two spacing sheets inside the fold at 20 °C. An evaluation of the extent of stripping of the coatings from the test coated substrates was performed; following the stripping of the tape over the part of the coated substrate evaluated, and is reported using the following scale:

◎: no stripping

◎ - O: stripped area of less than 10 %

O: stripped area of 10 % or greater, but less than 50 %

Δ: stripped area of 50 % or greater, but less than 80 %

X: stripped area of 80 % or greater.

4.2.2 Secondary Folding Adhesion Test

The test sheets were immersed in boiling water for 2 hours, and were then allowed to stand for one day. Afterward, a test was performed in the same manner as the primary folding adhesion test. The reporting scale was the same as for the primary folding adhesion test.

4.3 Coin Scratching Test

A copper coin approximately the size of a U.S. quarter dollar (a Japanese 10-yen coin) was positioned at an angle of 45 degrees relative to each test sheet, and this coin was rubbed across the coating film at a constant speed under a load of 3 kilograms. The susceptibility of the coating film to scratching was then evaluated and is reported using the following scale:

◎: 0 % exposure of any part of the substrate under the primer

◎ - O: less than 10 % exposure of any part of the substrate under the primer

O: exposure of 10 % or greater, but less than 50 %, of any part of the substrate under the primer

Δ: exposure of 50 % or greater, but less than 80 %, of any part of the substrate under the primer

X: exposure of 80 % or greater of any part of the substrate under the primer.

A summary of the test conditions used for the pre-paint aqueous treatment agents is shown in Table 1, and a summary of the coated sheet performance test results obtained with these pre-paint aqueous treatment agents is shown in Table 2.

Working Examples No. 1 through 13 in Table 1 show the coated sheet performance values for metal materials on which coating films were formed by applying and drying pre-paint aqueous treatment agents of the present invention. It may be seen that the

corrosion resistance, primary folding adhesion, secondary folding adhesion and coin scratching properties were all good. In Comparative Examples No. 1 through 11 in Table 1, the corrosion resistance, primary folding adhesion, secondary folding adhesion and coin scratching properties were all inferior. Accordingly, the contribution of the present invention to industry is extremely significant.

Table 1

| Identifier | Substrate Material | Pretreatment | Treatment Solution Used | Peak Metal Temperature During Drying, °C | Coating Weight, g/m ² |
|------------------------|--------------------|------------------------------|-------------------------|--|----------------------------------|
| Example 1 | GI | None | A | 70 | 0.4 |
| Example 2 | GI | None | B | 70 | 0.4 |
| Example 3 | GI | None | C | 70 | 0.4 |
| Example 4 | GI | None | D | 70 | 0.4 |
| Example 5 | GI | None | E | 70 | 0.4 |
| Example 6 | GF | None | A | 70 | 0.4 |
| Example 7 | GL | None | B | 70 | 0.4 |
| Example 8 | AL | None | C | 70 | 0.4 |
| Example 9 | GI | None | D | 120 | 0.4 |
| Example 10 | GI | None | E | 180 | 0.4 |
| Example 11 | GI | None | A | 70 | 1.0 |
| Example 12 | GI | Chemical Plating | A | 70 | 0.1 |
| Example 13 | GI | Phosphate Conversion Coating | B | 70 | 0.1 |
| Comparative Example 1 | GI | None | F | 70 | 0.4 |
| Comparative Example 2 | GI | None | G | 70 | 0.4 |
| Comparative Example 3 | GI | None | H | 70 | 0.4 |
| Comparative Example 4 | GI | None | I | 70 | 0.4 |
| Comparative Example 5 | GI | None | J | 70 | 0.4 |
| Comparative Example 6 | GI | None | K | 70 | 0.4 |
| Comparative Example 7 | GI | None | L | 70 | 0.4 |
| Comparative Example 8 | GI | None | M | 70 | 0.4 |
| Comparative Example 9 | GI | None | N | 70 | 0.4 |
| Comparative Example 10 | GI | Chemical Plating | I | 70 | 0.4 |
| Comparative Example 11 | GI | Phosphate Conversion Coating | J | 70 | 0.4 |

Table 2

| Identifier | Coated Substrate Performance Ratings | | | Coin Scratching | |
|------------------------|--------------------------------------|------------------|-----------|-----------------|--|
| | Corrosion Resistance | Folding Adhesion | | | |
| | | Primary | Secondary | | |
| Example 1 | ◎ | ◎ | ◎ | ◎-○ | |
| Example 2 | ◎-○ | ◎ | ◎ | ◎-○ | |
| Example 3 | ◎-○ | ◎ | ◎ | ◎-○ | |
| Example 4 | ◎-○ | ◎ | ◎ | ◎-○ | |
| Example 5 | ◎-○ | ◎ | ◎ | ◎-○ | |
| Example 6 | ◎ | ◎ | ◎ | ◎-○ | |
| Example 7 | ◎-○ | ◎ | ◎ | ◎-○ | |
| Example 8 | ◎-○ | ◎ | ◎ | ◎-○ | |
| Example 9 | ◎ | ◎ | ◎ | ◎-○ | |
| Example 10 | ◎ | ◎ | ◎ | ◎-○ | |
| Example 11 | ◎ | ◎ | ◎-○ | ◎-○ | |
| Example 12 | ◎-○ | ◎ | ◎ | ◎ | |
| Example 13 | ◎ | ◎ | ◎-○ | ◎ | |
| Comparative Example 1 | X | X | X | X | |
| Comparative Example 2 | X | X | X | X | |
| Comparative Example 3 | X | X | X | X | |
| Comparative Example 4 | Δ | Δ | X | Δ | |
| Comparative Example 5 | X | X | X | - X | |
| Comparative Example 6 | X | X | X | X | |
| Comparative Example 7 | Δ | X | X | X | |
| Comparative Example 8 | X | X | X | X | |
| Comparative Example 9 | X | X | X | X | |
| Comparative Example 10 | Δ | Δ | Δ | Δ | |
| Comparative Example 11 | Δ | Δ | Δ | Δ | |